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Tiangan Lian, Michael T. Whalen, Lana Wong

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Effects of Oxide Film on the Corrosion Resistance of Titanium Grade 7 in Fluoride-Containing NaCl Brines

Tiangan Lian, Michael T. Whalen, Lana Wong
Lawrence Livermore National Laboratory
7000 East Ave, L-631,
Livermore, CA 94550

ABSTRACT

The effects of oxide film on the corrosion behavior of Titanium Grade 7 (0.12-0.25% Pd) in fluoride-containing NaCl brines have been investigated. With the presence of a 0.6 μm thick oxide layer, the annealed Ti grade 7 exhibited a significant improvement on the anodic polarization behavior. However, the oxide film did not demonstrate sustainable corrosion resistance in fluoride-containing solutions.

INTRODUCTION

The excellent corrosion resistance of titanium alloys results from the formation of a very stable, continuous, highly adherent, and protective oxide film on the metal surface. Additionally, the protective oxide film can form spontaneously and instantly when fresh metal surfaces are exposed to air and/or moisture because titanium is highly reactive in nature and has an extremely strong affinity for oxygen. In the current design of the Yucca Mountain nuclear waste repository project, titanium grade 7 (UNS R52400) is chosen to construct the drip shield structure that diverts water drip and rock fall directly onto the waste packages. The titanium alloy drip shield will be exposed to various high temperature processes, such as welding, stress release annealing, and the heat radiated from the nuclear waste. These thermal processes can promote the formation of an oxide film on titanium grade 7. This goal of this study is to understand how the oxide film affects the corrosion behavior of Ti grade 7, particularly in fluoride-containing brines.

The effect of fluoride on the corrosion of Ti and Ti alloys has been extensively studied by researchers for industrial and bio-medical applications.^{1,2,3,4,5} In our previous study of fluoride effects, the electrochemical corrosion behavior of Ti grade 7 in fluoride-containing NaCl brines was studied at pH values of 4, 8, and 11.⁶ Fluoride altered the anodic polarization behavior significantly in the solutions at all three pH values. With presence of 0.1M $[\text{F}^-]$ in NaCl brines, no passivity was observed in the acidic (pH at 4) solution, and at pH 8, the fluoride reduced the passivity of Ti grade 7, as shown in Figure

1(a) and Figure 1(b) respectively. Under acidic conditions, fluoride caused active corrosion in Ti grade 7 and the addition of Pd in Ti grade 7 did not ennoble the titanium alloy in acidic, fluoride-containing environments. The corrosion of Ti grade 7 was increased by three orders of magnitude when a 0.1 mol/L fluoride was added to the NaCl brines at pH 4, as shown in Figure 2. By increasing the solution pH to 8 and above, fluoride enhancement in the corrosion rate of Ti grade 7 was drastically reduced to be minimal.

It is believed that the thermal oxide film on the titanium surface can be protective when titanium is heated in air at temperatures of 600 to 800°C.⁷ The thermal TiO₂ film improves the corrosion resistance of titanium in dilute reducing acids, as well as reduces the absorption of hydrogen under cathodic charging.⁸ However, there is little data available on the effects of the thermal oxide film on the corrosion of titanium grade 7 in fluoride-containing brines. This paper includes our recent experimental results from the testing of annealed Ti grade 7 in fluoride-containing NaCl brines.

EXPERIMENT PROCEDURES

Table 1 lists the chemical composition of the wrought Ti grade 7 material provided for this study.

Table 1. Composition of Ti Grade 7 (heat# P914) specimens.

Elements	C	Fe	N	O	H	Pd	Ti
Concentration (wt%)	0.02	0.07	0.01	0.11	0.001	0.12	Bal.

The disc specimens, 15 mm in diameter and 3 mm in thickness, were machined by the original supplier. Specimens were wet ground with 600-grit SiC paper, and then ultrasonically cleaned in de-ionized water. For testing oxide effects, the ground disc samples were treated for stress relief annealing in an oven at 593°C for 3 hours, and then air cooled. After annealing, the Ti grade 7 samples formed an oxide layer with a thickness of approximately 0.6 µm, while the Ti grade 7 samples that were not annealed had an oxide layer thickness of approximately 0.03 µm.

A three-electrode cell, with a capacity of 1 liter, was used for all experiments. Approximately 900 mL of electrolyte were used in each test. The disc specimens were placed in an ASTM G5 type flat specimen holder with an exposed surface area of approximately 0.75 cm². A silver/silver chloride (Ag/AgCl, prefilled with 4 M KCl saturated with AgCl) reference electrode was used for measuring the potential of the working electrode. A solution bridge with a luggin probe was used to maintain an ionic conductive path between the working electrode and the reference electrode, while a cooling jacket was used to maintain the reference electrode at near room temperature. A platinum (Pt) rod or sheet was used as a counter electrode. To maintain the test solution at 95°C, the electrochemical cell assembly was placed in a circulation temperature bath. An Allihn condenser was used to prevent solution loss through evaporation. The

electrochemical polarization measurements were conducted through a commercial potentiostat integrated with a computer and the companion software.

The test solutions used in this study were 1 mol/L (or 1 M) NaCl brines. To study the effects of fluoride, 0.1 mol/L NaF was added into the NaCl brines. The solution pH was adjusted prior to each test to pH values of 4, 8, and 11. The test temperature was 95°C. N₂ gas purging was used to de-aerate the test solutions. Gas purging began at least one-half hour before the specimens were placed into the solution.

Short-term electrochemical testing was first used to evaluate the effects of surface oxide on the corrosion behavior of Ti grade 7 in fluoride-containing environments. In these tests, Ti grade 7 specimens were stabilized for 1 hour in the test solution, and an anodic potentiodynamic polarization measurement was performed. A potential scan rate of 600 mV per hour was used for all polarization measurements.

A longer-term type of testing was also used to evaluate the sustainability of corrosion resistance of Ti grade 7 as well as the effects of fluoride on the corrosion behavior of Ti grade 7 in NaCl brines. In these tests, Ti grade 7 specimens were exposed to the test solution for up to 1 week. The corrosion potential (E_{corr}) was monitored, and polarization resistance (R_p) measurements were performed at various time increments during the exposure time line.

RESULTS AND DISCUSSION

Anodic Polarization Behavior

Figure 3 shows the anodic polarization curves on both freshly grounded Ti grade 7 (curves with solid markers) and annealed Ti grade 7 (curves with open markers) in NaCl brines with fluoride (curves with square markers “■” or “□”) and without fluoride (curves with circle markers “●” or “○”) at pH 4 and 95°C. The polarization results showed that the oxide film formed on the annealed metal noticeably and improved the anodic polarization behavior. In the 1M NaCl + 0.1M NaF solution at pH 4 and 95°C, the annealed Ti grade 7 showed a drastic decrease in anodic current by nearly two orders of magnitude, as compared to the freshly-ground Ti grade 7 base material. Although this decrease was not enough to passivate the Ti grade 7 surface, the dissolution rate of the oxide film in acidic fluoride-containing brines was evidenced to be much slower. The enhanced corrosion resistance of annealed Ti grade 7 was also observed in acidic NaCl brines without fluoride, where the corrosion potential increased by nearly 500 mV.

Figure 4 shows the anodic polarization results from similar tests with only a pH change to 8. The oxide film of annealed Ti grade 7 increased the corrosion potential by approximately 500 mV in the solutions, with and without the addition of 0.1M NaF. In the 1M NaCl + 0.1M NaF solution at pH 8 and 95°C, the annealed Ti grade 7 improved the anodic polarization behavior in the potential range up to 2 V (vs. Ag/AgCl). This observed improvement in the polarization behavior could be significant. In Ti grade 7 base metal, the presence of fluoride in the solution caused a “break-down” like feature in the anodic polarization behavior. If this “break-down” phenomenon were related to the

susceptibility of localized corrosion, then the oxide film of annealed Ti grade 7 appeared to diminish that susceptibility.

Figure 5 shows the polarization test results for the pH 11 solutions. The results clearly show that the oxide film of the annealed Ti grade 7 completely diminished the fluoride effects.

Long-Term Corrosion Potential and Corrosion Rate

Based on the anodic polarization behavior, the oxide film formed on the Ti grade 7 surface during the annealing treatment exhibited improved anodic polarization properties in fluoride-containing solutions. The sustainability of this oxide film effect was evaluated by immersing the samples in the solutions for up to 1 week. The change in corrosion potential and corrosion rate was used to assess the long-term behavior of annealed Ti grade 7. The corrosion rate was expressed as $1/R_p$, based on the results of polarization resistance measurements.

Figure 6(a) shows the corrosion potentials of the annealed Ti grade 7 and the freshly grounded Ti grade 7 samples, in NaCl solutions at pH 4 and 95°C, with and without the addition of 0.1M NaF. In the 1M NaCl + 0.1M NaF solution at pH 4 and 95°C, the annealed Ti grade 7 had a corrosion potential approximately -0.6 V (vs. Ag/AgCl), about 100 mV more noble (or higher) than the freshly ground Ti grade 7 base metal. The corrosion potential of the base metal and the annealed Ti grade 7 in fluoride-free NaCl solution was near 0 V (vs. Ag/AgCl). The presence of fluoride resulted in approximately 600 mV more active in corrosion potential. Throughout the 1-week immersion, the corrosion potentials appeared to be fairly stable and thus, implies that no surface Pd enrichment or corrosion potential ennoblement occurred.

Figure 6(b) shows the corrosion rates of annealed Ti grade 7 and freshly ground Ti grade 7 base metal in NaCl solutions at pH 4 and 95°C, with and without the addition of 0.1M NaF. The annealed Ti grade 7 exhibited significant improvement in reducing the corrosion rate in the 1M NaCl + 0.1M NaF solution at pH 4 and 95°C by 2 orders of magnitude.

The corrosion of freshly ground Ti grade 7 base metal in the acidic, fluoride-containing solution was severe and the metal surface was corroded uniformly by the fluoride-containing electrolyte as shown in Figure 7. Although annealed Ti grade 7 showed a much lower corrosion rate in acidic, fluoride-containing NaCl solution, the SEM examination on the test specimen revealed extensive corrosion. Figure 8 shows the surface of the annealed Ti grade 7 sample after 1-week immersion in the 1M NaCl + 0.1M NaF solution at pH 4 and 95°C. The SEM image shows that the corrosion attack was not by uniform thinning of the surface layer. Instead, the initial attack appeared to be penetration of the surface oxide film in numerous sites scattered on the specimen surface. After reaching underneath Ti grade 7 substrate, the corrosion appeared to be more preferential along the grain boundaries, even though attack was also observed on the facets of grains. With preferential attack on the grain boundaries, the corrosion penetration and propagation could be underestimated due to the relatively small corrosion rate measured electrochemically.

Figure 9(a) shows the corrosion potentials of the annealed Ti grade 7 and the freshly ground Ti grade 7 samples in NaCl solutions at pH 8 and 95°C, with and without the addition of 0.1M NaF. The corrosion potential of the annealed Ti grade 7 in the pH 8 solutions containing 0.1M NaF was ennobled by the oxide layer by approximately 400 mV in the first 4 days of immersion. However, this ennoblement could not be sustained after 4 days. The post-test examination did not show any noticeable corrosion on the annealed Ti grade 7 surface that could be linked to this loss of nobility. The repeat test showed a similar result. Figure 9(b) shows the corrosion rate ($1/R_p$) results. Fluoride had no effect on the corrosion rate of the annealed Ti grade 7 in the first 4 days, but imparted a significant increase in the corrosion rate after 4 days where the corrosion rate of the annealed Ti grade 7 was similar to the corrosion rate measured on the freshly ground Ti grade 7 base metal.

At pH 8, corrosion of the freshly ground Ti grade 7 base metal in the fluoride-containing solution was observed only under the Teflon gasket as shown in Figure 10. Although the freshly ground base metal had only a thin ($\sim 0.03 \mu\text{m}$) oxide film, it appeared to be adequately protective except in the areas that the oxide film was damaged by the gasket. Surface examination on the annealed Ti grade 7 after 1-week immersion in the pH 8 fluoride-containing solution did not reveal noticeable corrosion even though the electrochemical measurement data showed an increase in corrosion after 4 days of immersion. Although immersion tests longer than 1 week have not been performed yet, it is reasonable to speculate that corrosion could be observable in the annealed samples if given an adequately long immersion time.

Acidic, Fluoride-Containing Waters in the Repository Environment Are Unlikely

It is important to point out that the selection of the test environments does not reflect the realistic environments that might be present in the repository. The repository environment is not expected to see high fluoride-containing brines with an acidic pH.

For the environmental conditions at the drip shield and waste packages that are of low relative humidity, the waters that come in contact with the engineered barrier system components will be brines which form either through seepage water evaporative concentration or through salt and/or dust deliquescence, and can be divided into three general types⁹:

- High calcium chloride, pH ranging acidic to neutral,
- High sulfate, neutral pH,
- High carbonate, alkaline pH.

All three brine types that are relevant to Yucca Mountain will contain relatively significant quantities of chlorides and nitrates, whether derived from the evaporation of seepage water or deliquescence of salts in dust. Due to the presence of calcium in CaCl_2 brines, and Mg in high-sulfate brines, significant fluoride presence is not possible in both high- CaCl_2 and high-sulfate brines. Therefore in the repository environment, only high carbonate brines can potentially contain significant level of fluorides.

SUMMARY

It has been demonstrated that the corrosion resistance of Ti grade 7 in fluoride-containing solutions can be improved by the formation of a thermal oxide film on the surface. However, the oxide film could not completely prevent the fluoride-enhanced corrosion, only delay or slow it down. Under acidic conditions, the annealed Ti grade 7 was attacked by fluoride-containing NaCl brines even though the attack was much less severe when compared to the attack on the freshly ground Ti-grade 7 without a thermal oxide film.

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REFERENCES

1. TIMET Company Report: "Corrosion Resistance of Titanium Information". Titanium Metals Corporation: <http://www.timet.com/core sistframe.html>T. 2004.
2. J. J. Kelly, "The Influence of Fluoride Ions on The Passive Dissolution of Titanium". *Electrochimica Acta*, Vol. 24, pp. 1273-1282, 1979.
3. W. Wilhelmsen and A. Peder Grande, "The Influence of Hydrofluoric Acid and Fluoride Ion on The Corrosion and Passive Behavior of Titanium". *Electrochimica Acta*, Vol. 32, No. 10, pp.1469-1474, 1987.
4. L. Reclaru and J. M. Meyer, "Effects of Fluorides on Titanium and Other Dental Alloys in Dentistry". *Biomaterials* 19 (1998), pp. 85-92.
5. C. S. Brossia and G. A. Cragolino, "Effects of Environmental and Metallurgical Conditions on the Passive and Localized Dissolution of Ti-0.15%Pd". *Corrosion*, Vol. 57, No. 9, pp. 768-776, 2001.
6. T. Lian, M. T. Whalen, and L. Wong. "Corrosion Behavior of Titanium Grade 7 in Fluoride-Containing NaCl Brines". Paper #723. The 206th Meeting of The Electrochemical Society, October 3-8, 2004. Honolulu, HI.
7. R. W. Schutz and D. T. Thomas. "Corrosion of Titanium and Titanium Alloys". ASM handbook, Vol.13, 1987".
8. R. W. Schutz and L. C. Covington. *Corrosion*, Vol 37 (No. 10), Oct 1981, p 585-591.
9. BSC 2004. "KTI Report Appendix A: Credible Range of Brine Water Chemistry and Consistency Between Corrosion Testing Environments and Models (Response to CLST 1.01, TSPAI 3.12, TSPAI 3.13, and GEN 1.01 (Comments 50, 113, 118, 122, AND 124))". Las Vegas, Nevada: Bechtel SAIC Company.

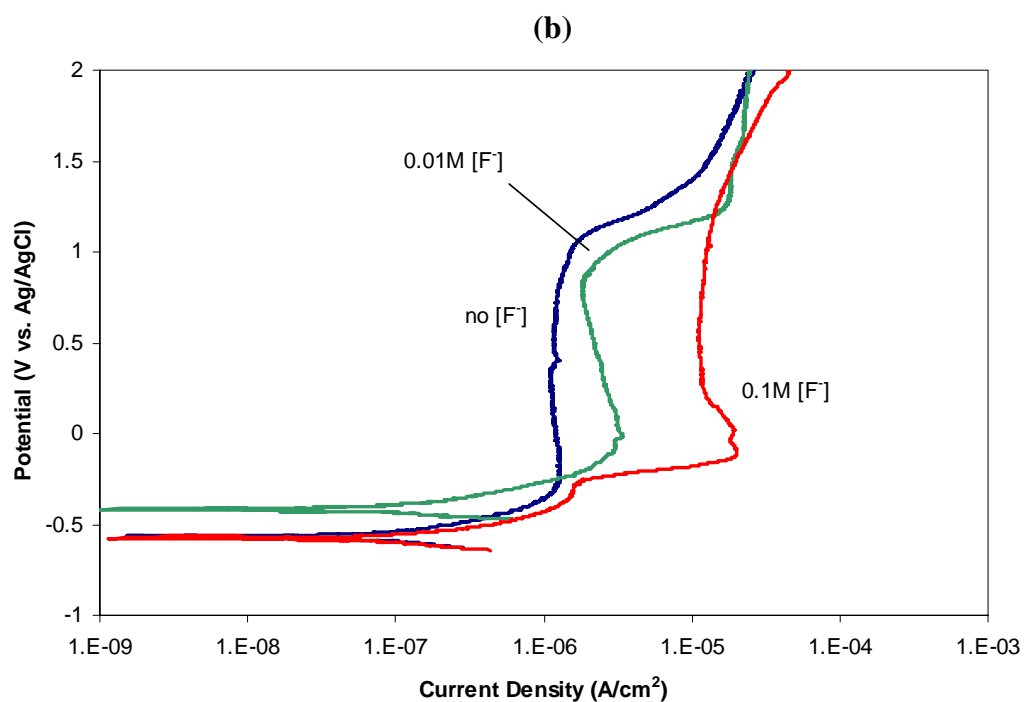
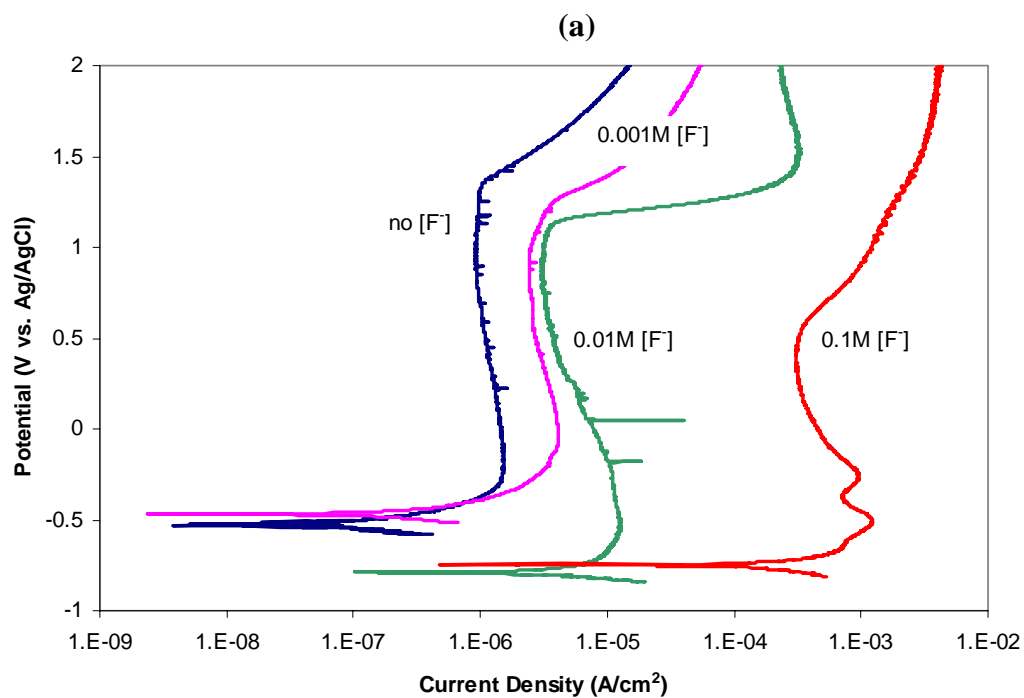


Figure 1. Anodic polarization curves shifted to right as increasing fluoride concentration in 1 M NaCl brines at (a) pH 4, and (b) pH 8, respectively. All tests were conducted at 95°C, and de-aerated with N₂.

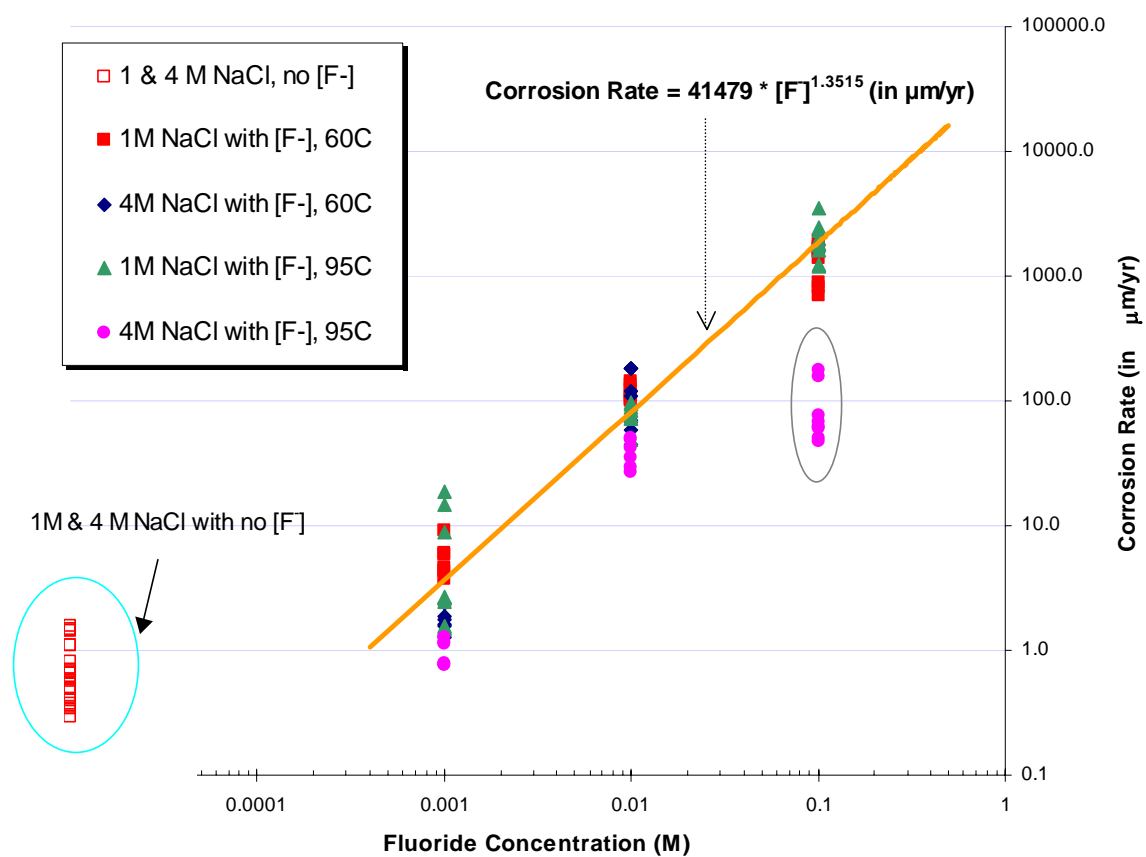


Figure 2. Fluoride effect on the corrosion rate of Ti grade 7 in acidic 1M & 4M NaCl brines at pH 4, 95°C and de-aerated with N₂.

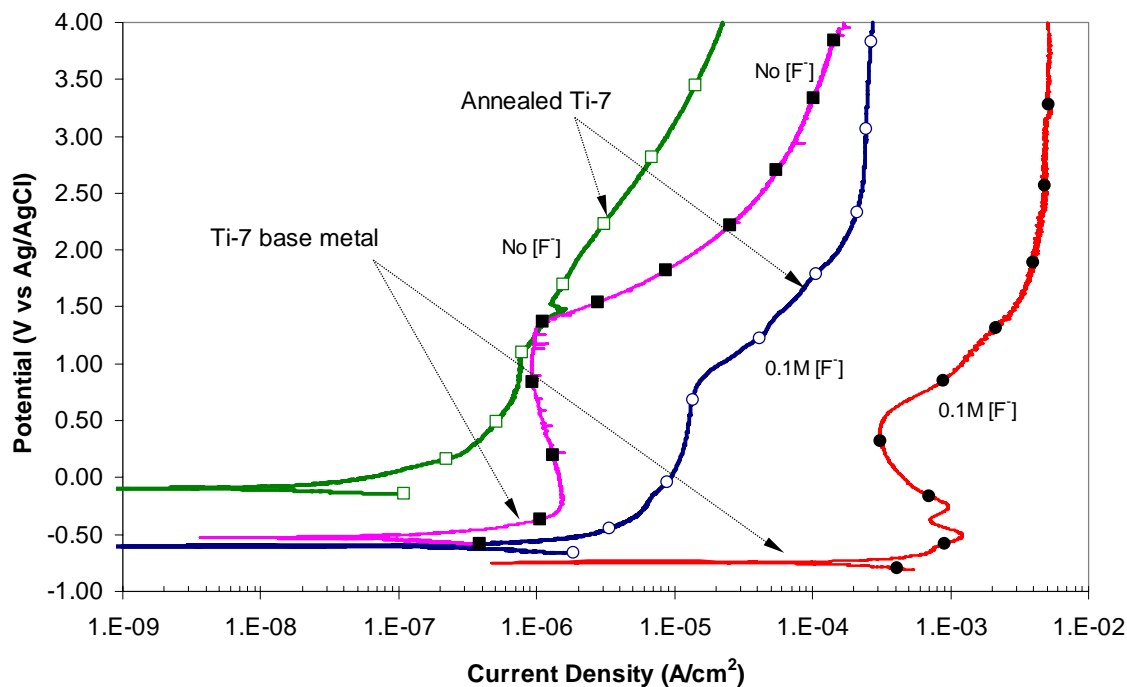


Figure 3. Anodic polarization behavior of both annealed and freshly ground Ti grade 7 in 1M NaCl brines with and without the fluoride, at pH 4, 95°C and de-aerated with N₂.

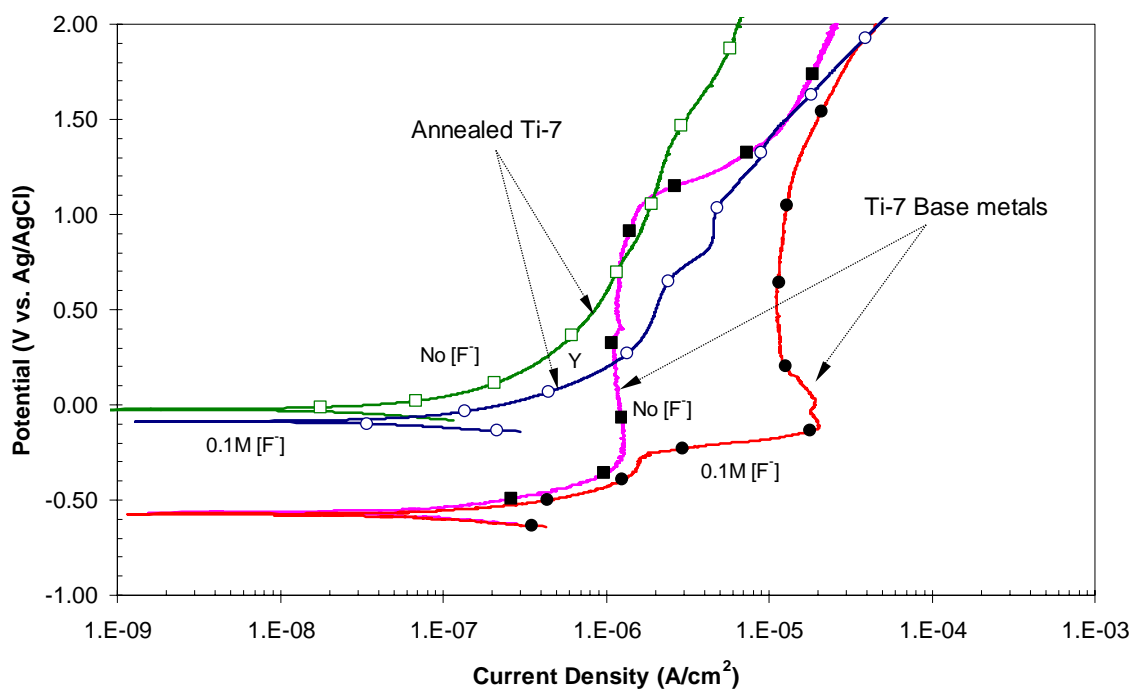


Figure 4. Anodic polarization behavior of both annealed and freshly ground Ti grade 7 in 1M NaCl brines with and without the fluoride, at pH 8, 95°C and de-aerated with N₂.

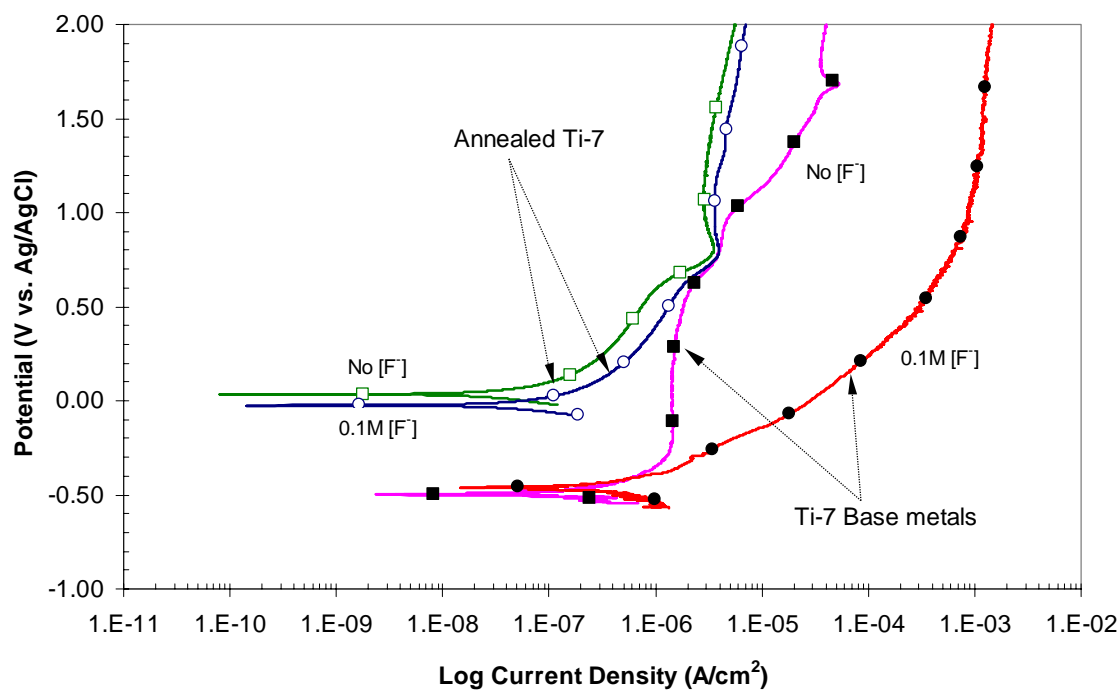


Figure 5. Anodic polarization behavior of both annealed and freshly ground Ti grade 7 in 1M NaCl brines with and without the fluoride, at pH 11, 95°C and de-aerated with N₂.

(a)

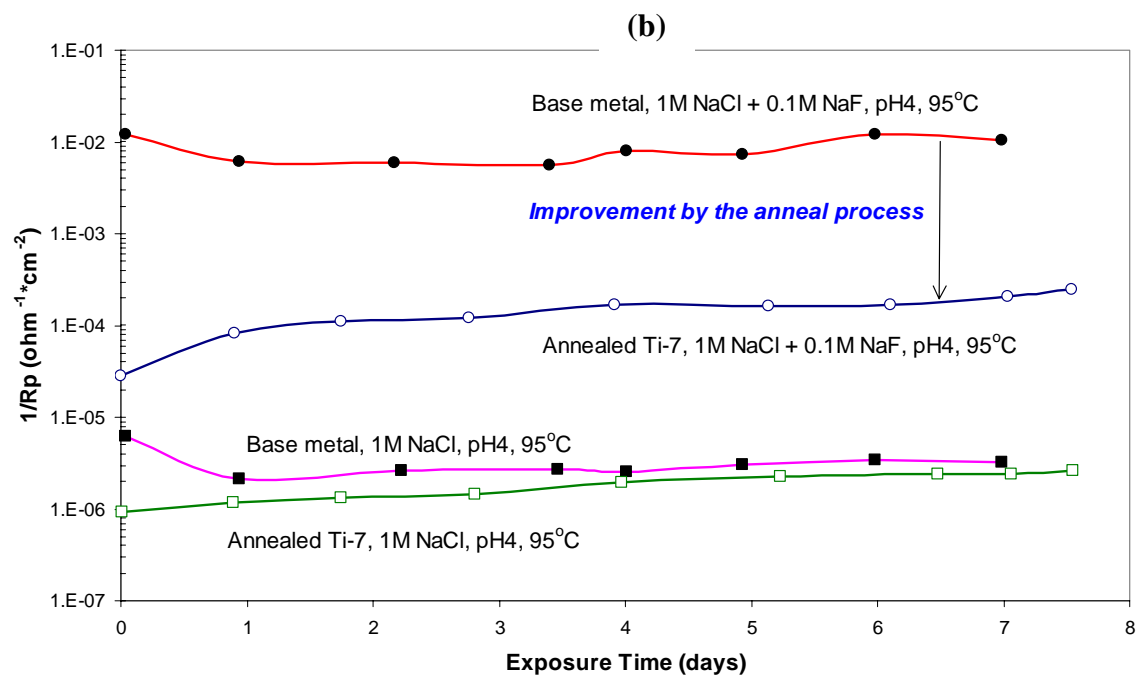
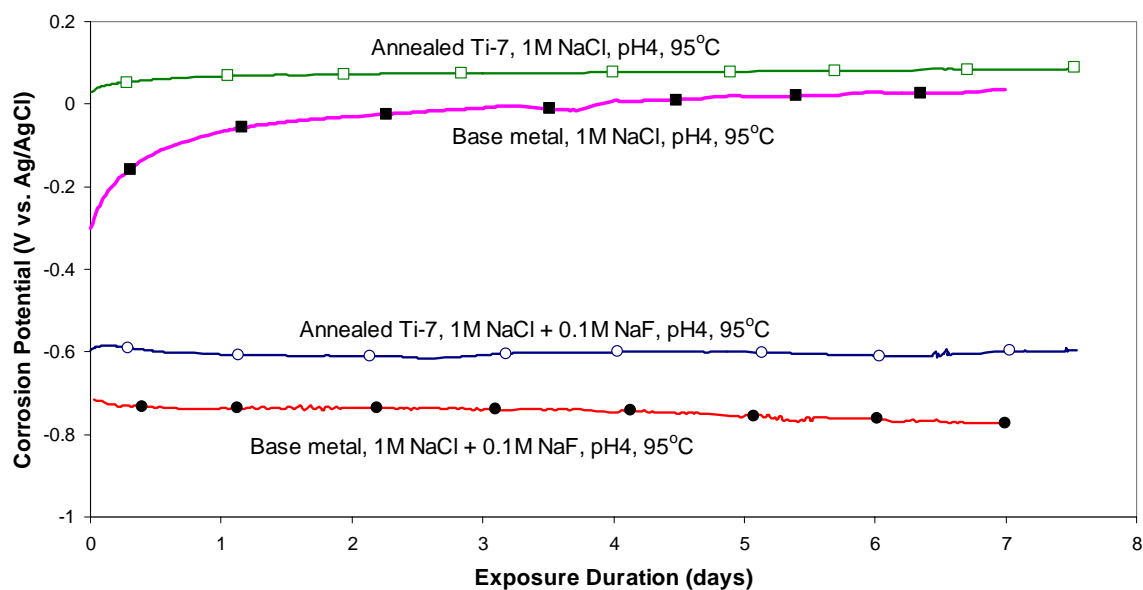


Figure 6. The corrosion potential, (a), and the corrosion rate, (b), of Ti grade 7 immersed in 1M NaCl brines with and without fluoride, at pH 4, 95°C and de-aerated with N₂.

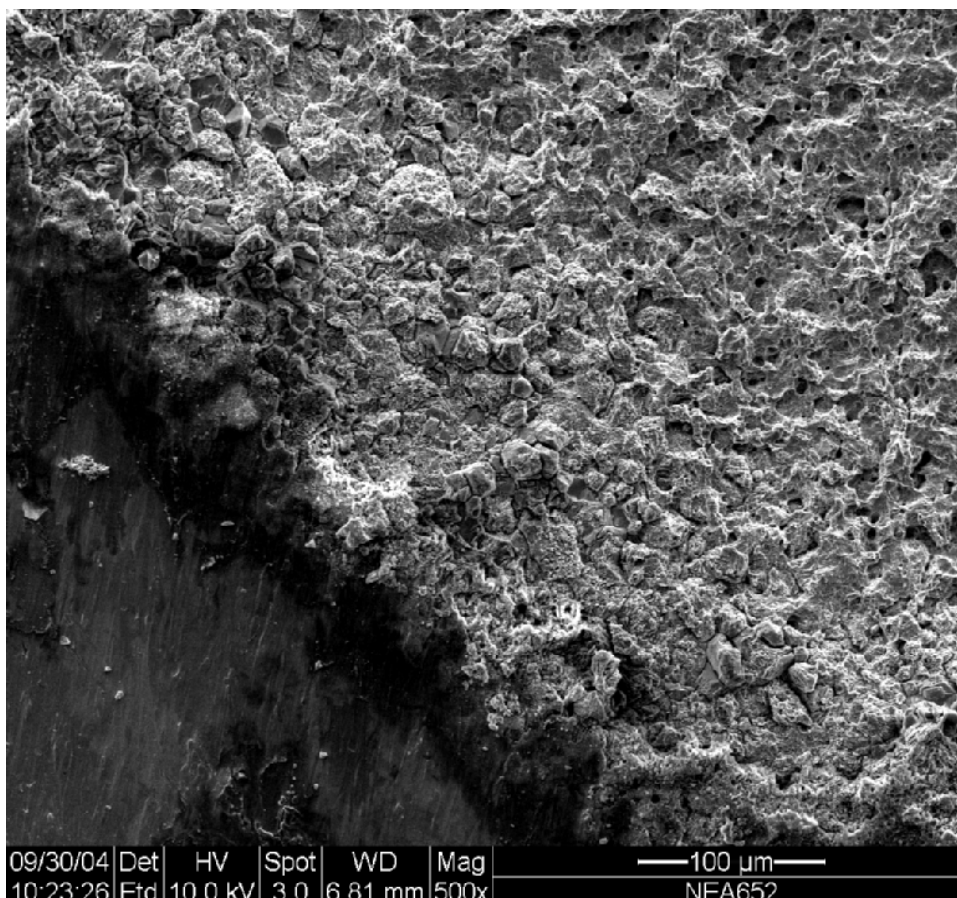


Figure 7. The corrosion surface of a freshly ground Ti grade 7 specimen after 1-week immersion in 1M NaCl + 0.1M NaF solution at pH 4, 95°C and de-aerated with N₂.

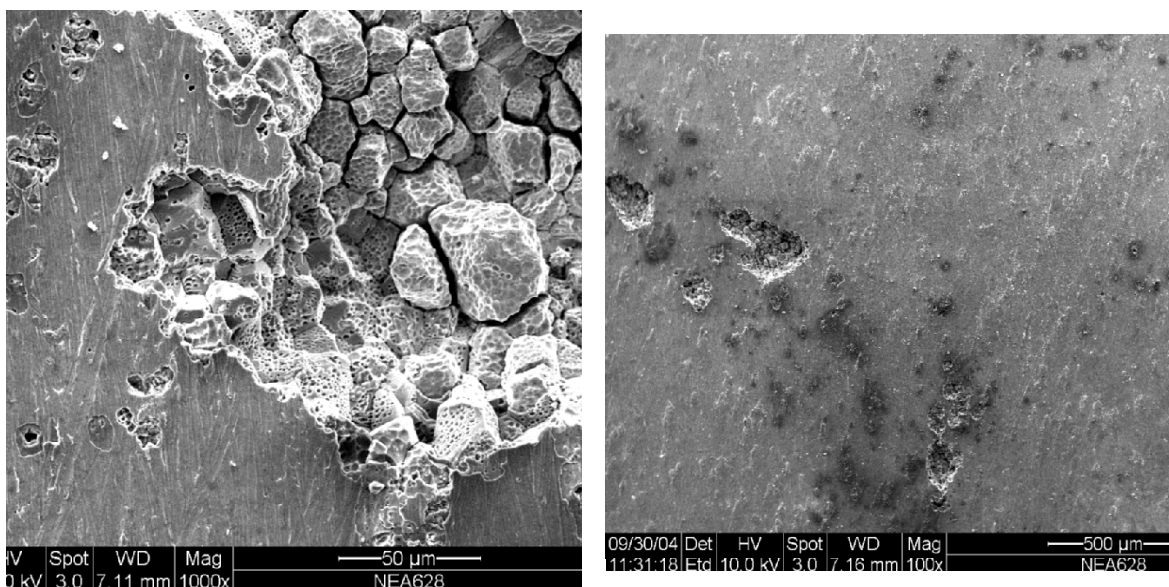


Figure 8. The corrosion surface of an annealed Ti grade 7 specimen after 1-week immersion in 1M NaCl + 0.1M NaF solution at pH 4, 95°C and de-aerated with N₂.

(a)

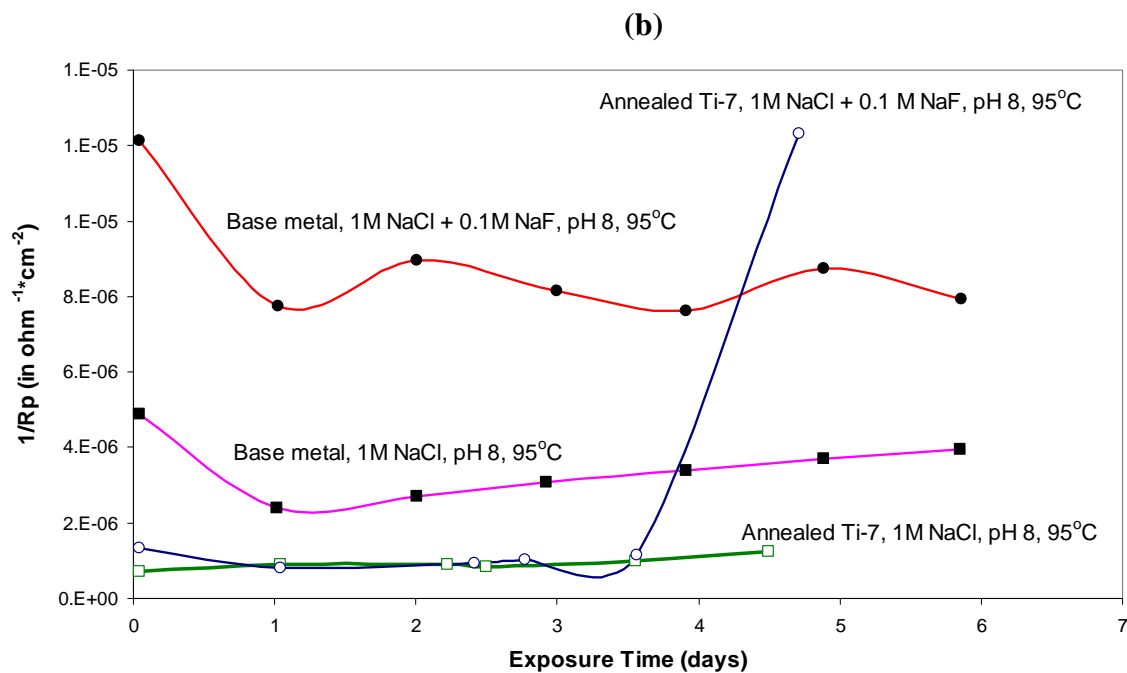
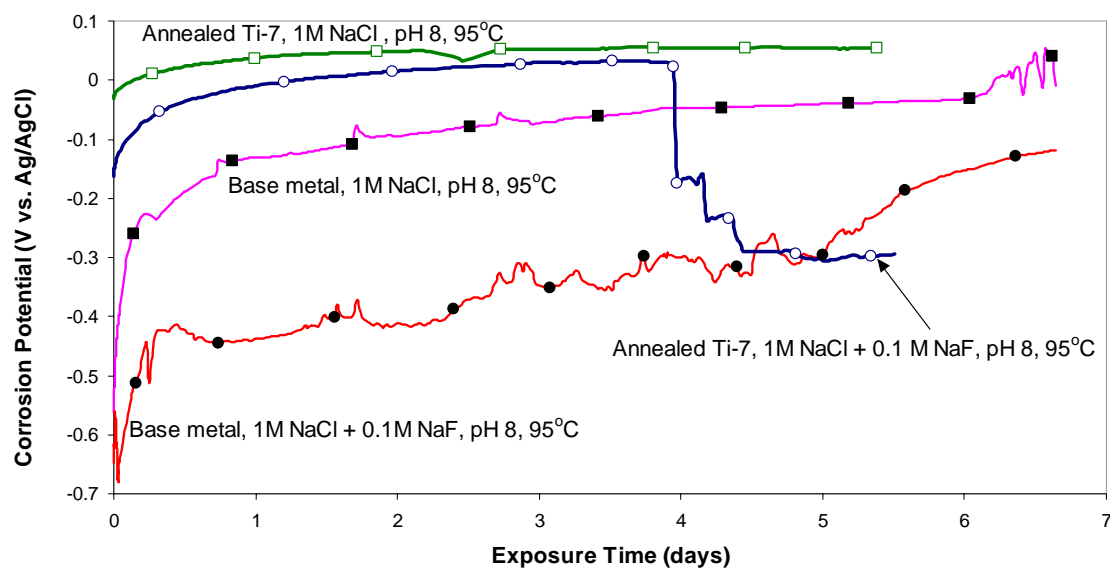


Figure 9. The corrosion potential, (a), and the corrosion rate, (b), of Ti grade 7 immersed in 1M NaCl brines with and without fluoride, at pH 8, 95°C and de-aerated with N_2 .

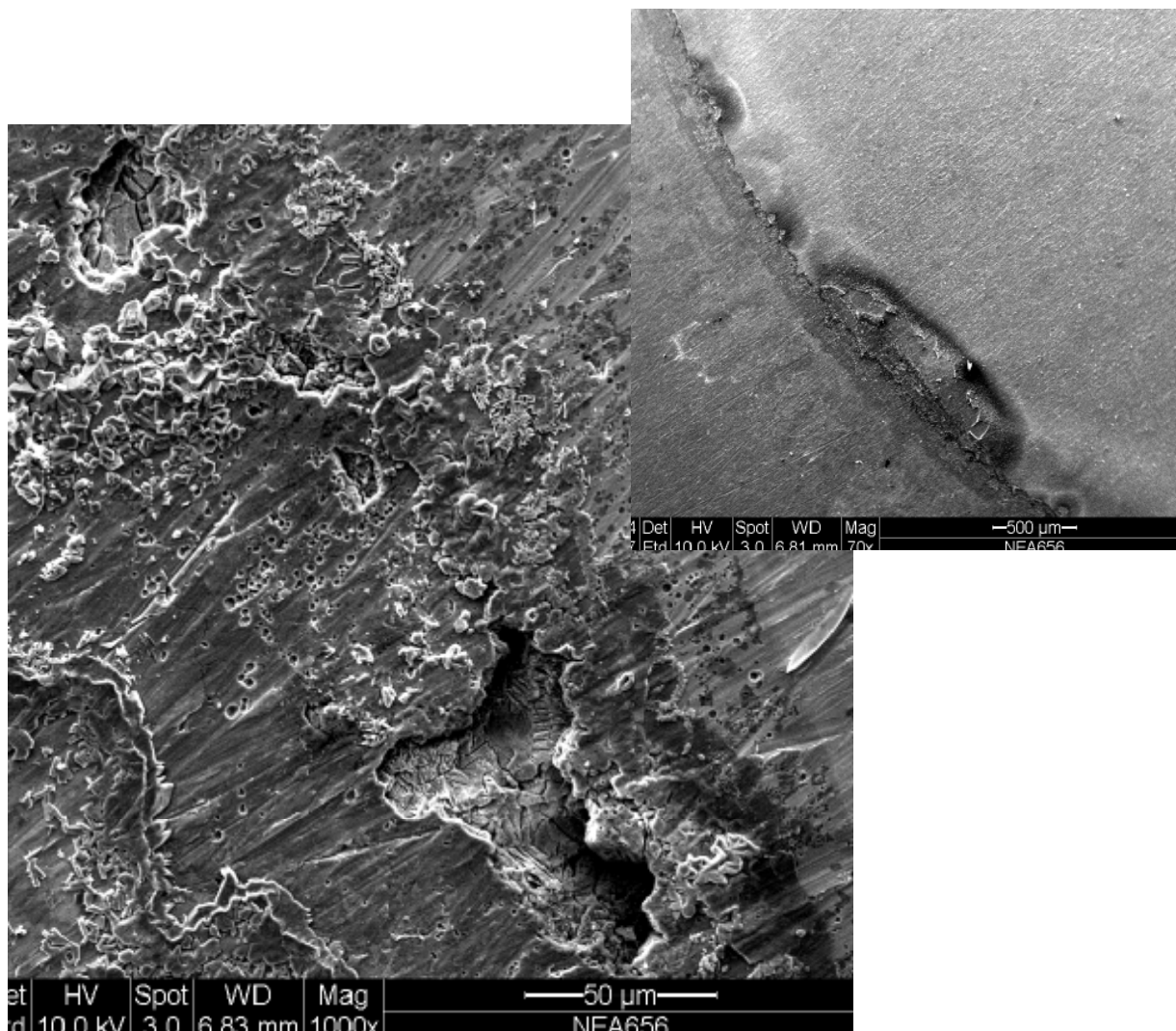


Figure 8. The corrosion surface of an annealed Ti grade 7 specimen after 1-week immersion in 1M NaCl + 0.1M NaF solution at pH 4, 95°C and de-aerated with N₂.